United States Department of Agriculture
Agricultural Marketing Service, Science & Technology
Pesticide Data Program

SOP No.: PDP-LABOP-10		Page 1 of 11
Title: Laboratory Procedures for Acute Dietary Risk Survey, "Organophosphates and Carbamates in Apples"		
Revision: 1	Replaces: 01/01/99	Effective: 05/01/99

1. Purpose:

To provide standard procedures for the receipt, preparation, storage, analysis, reporting, and disposal of USDA, AMS Pesticide Data Program (PDP) samples for the acute dietary risk survey, "Organophosphates and Carbamates in Apples".

2. Scope:

This standard operating procedure (SOP) shall be followed by the analytical laboratory conducting pesticide residue studies for the PDP Acute Dietary Risk Survey, "Organophosphates and Carbamates in Apples", the New York Department of Agriculture & Markets Food Laboratory (NY1). All samples should be shipped to this location. Monthly sampling rates are at 50 percent of normal State sample apportionment for commodities, yielding a total of 32 samples/month as follows:

CA - 7	NY - 5
CO - 1	OH - 3
FL - 4	TX - 4
MD - 2	WA - 2
MI - 3	WI - 1

3. Outline of Procedure:

6.1 Sample Receipt
6.2 Sample Preparation
6.3 Sample Storage
6.4 Sample Analysis
6.5 Data Reporting
6.6 Single Serving Analytical Requirements
6.7 Sample Disposal

4. References:

USDA/EPA Meeting, April 19, 1999
PDP Federal/State Meeting, December 1-3, 1998

USDA, AMS PDP Program Plan, January 1999 - June 1999

USDA, AMS Organophosphate/Apples Acute Dietary Risk Survey Protocol, 10/1/98

5. Summary:

For each sample, ten apples are randomly selected and labeled A-J. Each apple is cut into 8 slices, with alternate slices selected to comprise two halves for each apple. One half of each of the ten apples are combined and analyzed as a composite sample, with data reported under the standard sample identification number and no IDNO_SUB. The remaining half of the apple labeled "A", also referred to as the tenth apple, is analyzed individually and data are reported under the standard sample identification number, with "A" entered into the IDNO_SUB field in the RDE data tables. If the composite sample contains ≥ LOQ for azinphos methyl and/or ≥ LOQ for chlorpyrifos, the remaining nine halves are analyzed individually with their IDNO_SUB values reported as B-J.

6. Specific Procedures:

These operating procedures provide minimum requirements for the receipt, preparation, storage, analysis, reporting, and disposal of USDA, AMS, PDP samples for the acute dietary risk survey, "Organophosphates and Carbamates in Apples". Each participating laboratory shall, as part of their internal laboratory SOPs, have written instructions providing specific details concerning how these procedures have been implemented in that laboratory.

6.1 Sample Receipt

a. Each sample received shall be comprised of five pounds of apples. The laboratory shall randomly select ten individual apples weighing at least 150 grams or 1/3 lb. each for analysis, in order to provide ample analytical portion for single serving analyses. If samples do not contain large enough apples, do not pair apples for analysis. Please notify Residue Branch.

b. Those samples, or portions thereof, received in a damaged condition shall be discarded and not analyzed. Condition and disposal shall be documented on the Sample Information Form (SIF).

1. If a sample bag should split open during shipment, causing a portion

of the sample to come in contact with a portion(s) of another sample(s), the affected samples shall be discarded and not analyzed. The date and time received shall also be documented on the SIF.

2. The bags shall not be opened, but shall be visually inspected for any deteriorating condition (e.g., leaking of paper bag) which would make the sample inedible.

c. The composite shall have the standard sample identification number. Remaining individual halves shall be labeled with IDNO_SUB A-J. The commodity identification section of the sample identification number shall be "AP" for the composite and all individual halves.

d. Each laboratory shall maintain a log of samples received. Suggested methods are:

1. Each sample shall be logged into a bound notebook with ink. Mistakes shall be crossed out (one single line, no whiteout) and corrections dated and initialed. Minimum information for the logbook includes sample numbers, date, and time received (unless documented on the SIF) and recipient name/initials. Other information may include commodity type, reference to the analytical method, results, and date when results were reported.

2. Computer logs are also acceptable. The laboratory shall assure that verified hardcopies are generated on a routine basis and that electronic storage of data follows acceptable practices. Refer to PDP SOP DATA-05.

6.2 Sample Preparation

a. Wash apples per PDP SOP LABOP-03. Remove stem, if present. Core each apple using a commercial corer that divides the apple into 8 equivalent sections.

b. For each of the ten apples, select alternate sections. For nine of these apples,

place 4 of the 8 sections in a suitable freezer container and label B-J. Store labeled subsamples at 0° C or less. For the tenth apple, A, set aside four of the alternate eighths for single serving analysis. Combine the remaining four eighths with those reserved from the first nine halves for the composite.

c. Mechanically chop halves comprising the composite just until a visually homogeneous mixture is attained.

d. For tenth half apple A,

1. Homogenize in a food chopper which will ensure a finely chopped, homogeneous mixture.

Or

2. Place sample in labeled Ziplock freezer bag and store at 0°C or less. Extract entire sample, making appropriate adjustments to extraction solvent and process controls.

6.3 Sample Storage

An adequate portion of the homogenized composite sample, as processed in 5.2.c, shall be held in reserve if re-analysis and/or confirmation is needed. This portion shall be distributed among several small containers (polypropylene or styrofoam recommended) rather than one large container and stored at 0°C or less. The laboratory internal SOP shall specify "adequate portion" and distribution.

The remaining homogenized individual sample shall be retained in an appropriately sized, labeled container and stored at 0°C or less.

6.4 Sample Analysis

a. Weighing of Analytical Portion

An appropriate amount of homogenized sample shall be weighed for analysis. The laboratory internal SOP shall define the sample weight and the necessary

precision which, for a 50 gram sample shall not be more than +/- 0.25 grams.

b. Sample Set Requirements

A sample set is the group of samples which are spiked individually with the designated process control and extracted on a single day along with the required QC samples. Each set shall consist of no more than 20 analytical samples, where an analytical sample is defined as either a composite or individual. Required QC samples per set consist of a reagent blank, apple matrix blank, and apple matrix spike(s).

The matrix spike(s) shall be spiked at approximately 2xLOQ and shall contain at least the following compounds (marker organophosphates and carbamates): azinphos methyl, diazinon, dimethoate, ethion, carbaryl, and methomyl.

Each sample shall be spiked with the appropriate organophosphate and carbamate process controls at approximately 5xLOQ. All components of sample sets shall be subject to the sample analytical process as detailed in the method SOPs.

c. Analytical Requirements

Each composite plus the tenth half apple, A, shall undergo analysis for the identified organophosphate and carbamate compounds. See Table 1 and Table 2 for these listings.

Table 1. Required Organophosphates

Azinphos methyl	Fenamiphos sulfone
Chlorpyrifos	Malathion
Diazinon	Malathion oxygen analog
Diazinon oxygen analog	Methidathion
Dimethoate	*Oxydemeton methyl sulfone*

Omethoate	Parathion
Ethion	Parathion oxygen analog
Ethion monoxon	Parathion methyl
Ethion di oxon	Parathion methyl oxygen analog
Fenamiphos	Phosmet
Fenamiphos sulfoxide	

Table 2. Required carbamates

Carbaryl	Oxamyl	Methomyl

Standards for italicized compounds will be available through the US EPA Standards Repository. Please contact Francis (Dick) Griffith, EPA, Fort Meade, MD, fax (410) 305-2999, to procure standards. Some italicized compounds are also available through ChemService or Crescent and can be ordered on the PDP blanket purchasing agreement account.

All new compounds and compounds added since apples were removed from the program shall undergo validation/evaluation requirements as specified in PDP SOP QC-07. All compounds requiring validation shall be considered as "related to the marker compounds" for validation purposes.

6.5 Data Reporting

a. Process control and marker matrix spikes for composites and individuals shall be subject to the criteria and reaction procedures set forth in PDP SOP QC-04 "Acceptability Criteria for Process Control and Fortification Recoveries".

b. No presumptive tolerance violation (PTV) reporting requirements, as specified in PDP SOP DATA-02 apply.

c. Data for composite samples and tenth half apples shall be transmitted

following established RDE procedures.

d. For each set the requirement for running single serving analyses shall be as follows:

If the results for the composite sample are ≥ LOQ for azinphos methyl (0.020 ppm) and/or ≥ LOQ for chlorpyrifos (0.010 ppm), then the sample identified will undergo single serving analysis of the nine stored subsamples of the composite for all identified organophosphates and carbamates (refer to 6.4.c).

6.6 Single Serving Analytical Requirements

All procedures as specified in this SOP apply to single serving samples, A-J, except the following:

a. The nine individual halves, B-J, shall be analyzed within the same set with appropriate QC samples. Two sets of nine may be combined in a single set (refer to section 6.4.b).

b. Samples are homogenized individually according to the procedures outlined in 6.2.d.

c. Any necessary single serving analyses (A-J) are not subject to the criteria specified in PDP SOP QC-04 and do not require confirmation as specified in PDP SOP DATA-02.

d. Reserve portions of subsample homogenates (A-J) may be discarded after weighing of analytical portion as the amount of reserve sample will be minimal. Disposal shall be documented (e.g., sample log, extraction worksheet) and shall contain a minimum of date of disposal, sample number, and initials of the individual who discarded the sample.

6.7 Sample Disposal

Homogenates of composites and individuals for each set shall be disposed of when all requirements for acceptability criteria have been met and results have been

successfully transmitted via RDE to USDA, AMS, Residue Branch. Disposal shall be documented (e.g., freezer log, sample log, extraction worksheet) and shall contain a minimum of date of disposal, sample number, and initials of the individual who discarded the sample.

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ELECTRONICALLY REPRODUCED SIGNATURES

Revision 1 April 21, 1999 Martha Lamont

- Updated reference section
- Added summary section to explain new protocol.
- Modified procedures section to reflect following protocol changes
  - Removal of 11th apple from sample
  - Analysis of half of each 10th apple
  - Reduction of azinphos methyl and chlorpyrifos triggers to respective LOQs